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ENTITLED MICROWAVE ROTATIONAL SPECTRA AND STRUCTURE

OF $HCN(CO_2)_3$

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# Microwave Rotational Spectra and Structure of $HCN(CO_2)_3$

By

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## Abstract

Microwave rotational spectra for $HCN(CO_2)_3$, $DCN(CO_2)_3$, $H^{13}CN(CO_2)_3$, $HC^{15}N(CO_2)_3$, $HCN(^{13}CO_2)_3$, and $HCN(^{18}OCO)(CO_2)_2$ have been observed with the pulsed Fourier transform method using the Flygare Mark II spectrometer. A symmetric top spectrum was observed with rotational constants, $B_o$ = 861.6392 (2) MHz, $D_J$ = 0.681 (5) kHz, $D_{JK}$ = 0.821 (12) kHz, for the main species. The spectra indicate a zero point vibrationally averaged geometry having $C_3$ symmetry with a cyclic $(CO_2)_3$ structure and an HCN along the symmetry axis with the N end closest to the $(CO_2)_3$ subunit. The $C_3$ symmetry is confirmed by observation of states only for K = +/- 3n, with n=0,1,2.... as predicted for all bosons off axis. The $(CO_2)_3$ subunit has a pinwheel configuration, as in the free trimer, and the three carbons lie in a plane which is 3.7580 Å below the c.m. of the HCN. The C-C distance in this subunit is 3.797 Å, 0.235 Å shorter than that observed for the free $(CO_2)_3$ trimer. The oxygens in the $(CO_2)_3$ pinwheel are rotated out of the C-C-C plane by 36.4°, as determined from an inertial analysis, with the inner O's being rotated away from the HCN. The O's are also rotated in the C-C-C plane by 38.2° away from $C_{3v}$ symmetry. The HCN has an average torsional angle of 10.3°, as determined by isotopic substitution, and an observed $\chi_{cc}$ value of -3.891 MHz. The N (HCN) to C ($CO_2$) distance is 4.3507 Å, as compared to 3.00 Å in the $HCN\text{-}CO_2$ T-shaped dimer.

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## INTRODUCTION

The ground vibronic state structure of a cyclic $CO_2$ trimer has been recently reported.[1] By symmetry, it has no permanent dipole moment and is consequently inaccessible to rotational spectroscopy. It was characterized, by means of near infrared laser spectroscopy, as a planar pinwheel trimer with $C_{3h}$ symmetry. Two parameters are needed to describe the geometry of such a trimer, but only one, the C-C distance, was obtained directly.[1] To find the pinwheel angle, $\beta$, isotopic substitution is required. However, a theoretical value was determined for $\beta$ by placing the known electrical quadrupole moment of $CO_2$ on each C and minimizing the electrostatic energy as a function of $\beta$.

Herein we report rotational constants and the ground vibronic state structure for a tetramer composed of the cyclic $(CO_2)_3$ with the N of the HCN weakly attracted to the C's of the $(CO_2)_3$. By using $^{13}CO_2$ and $HCN(CO_2)_2{}^{18}OCO$ (with the outer O substituted), we can characterize the structure of the cyclic $(CO_2)_3$ subunit in the $HCN(CO_2)_3$ tetramer. Such isotopic substitution was found to be useful in obtaining the structure of the $(CO_2)_2$ subunit in the recently characterized $HCN(CO_2)_2$ trimer.[2] By using $HC^{15}N$ and $H^{13}CN$, $R_{cm}$ and the torsional averaging of the HCN can be obtained.

Although a complete comparison of the cyclic $(CO_2)_3$ subunit in $HCN(CO_2)_3$ with free $(CO_2)_3$ awaits further experimental effort on $(CO_2)_3$ to determine the pinwheel angle $\beta$, it is possible to compare the C-C separation in $(CO_2)_3$. From the measured $^{14}N$ quadrupole coupling constant and the isotopically measured torsion of HCN, we also learn about the motion of HCN in the zero point vibrations and find evidence for charge redistribution effects at the N nucleus, and this is discussed in relation to the known structures of the T-shaped $HCN\text{-}CO_2$ dimer[3] and that of the trimer $HCN(CO_2)_2$. [2]

## EXPERIMENTAL

The microwave spectra of $HCN(CO_2)_3$, $HC^{15}N(CO_2)_3$, $H^{13}CN(CO_2)_3$, $DCN(CO_2)_3$, $HCN(^{13}CO_2)_3$, and $HCN(^{18}OCO)(CO_2)_2$ were measured using the Balle- Flygare Mark II spectrometer which has been described elsewhere.[4] The tetramer was found by accident as a set of $^{14}N$ hyperfine structure (hfs) centered at 5169.7 MHz was found while searching for rotational transitions of the $HCN(CO_2)_2$ trimer. The unexpected signal was optimized at a higher concentration of $CO_2$ than would be required for a transition of the trimer, and the species was identified as described in the next section.The carrier gas was neon 'first run' (Airco), a 70/30 mix of Ne and He, which we refer to as Ne. The concentrations of HCN (Fumico) and $CO_2$ (Linde) at the nozzle were 0.1 and 2 %, respectively, after coexpansion in 98% Ne. The backing pressure was 1.5 atm and the nozzle diameter was 1 mm.

The S/N ratio for a single free induction decay (FID) of the $J=2\rightarrow3$ transition of $HC^{15}N(CO_2)_3$ (no hfs) in Ne is about 20:1. This ratio was about a factor of 10 worse when Ar (Linde) was used as a carrier gas, and use of pure He gave signals approximately as strong as Ne.

The isotopic derivatives $HC^{15}N$ and $H^{13}CN$ were prepared by reacting orthophosphoric acid with $KC^{15}N$ and $K^{13}CN$ (Cambridge Isotope Laboratories), respectively; and deuterated orthophosphoric acid with KCN for DCN. The labelled $^{13}CO_2$ and 50% $^{18}O$ - $CO_2$ was purchased from Cambridge Isotopes.

## RESULTS AND ANALYSIS

Identification, hfs, and rotational constants

The hfs associated with the transition at 5169.7 MHz was indicative of a single $^{14}N$ nucleus with isotropic vibrational averaging about the molecular axis. The splittings of the hfs showed that it was a J=2→3, K=0 transition, and the hfs given in Table I was fitted to the usual Hamiltonian employed for a symmetric top or linear molecule[5] with a single quadrupole interaction along the symmetry axis. A set of hfs was then found at 4/3 x 5169.7 MHz, confirming a linear or symmetric top species with $B_o$ 861.3 MHz. Since the linear isomer HCN-$CO_2$ had already been characterized,[3] the obvious choice for this complex was a symmetric top of the form $HCN(CO_2)_n$, with n greater than 2.

The Hamiltonian H = H(R) + H(Q) was used to fit the spectra, and preliminary evidence for a symmetric top species was obtained by observing the hfs of K=0, J→J′ transitions, obtaining the line centers, and then fitting the line centers to the semi-rigid Hamiltonian,

$$E(J) = B_o 2J' - 4D_j J'^3 - 2D_{jk} J' K^2 \qquad (1)$$

where J′ is the upper rotational state, $B_o$ the rotational constant, and $D_j$ and $D_{jk}$ the usual first order centrifugal distortion constants. The line centers were determined by fitting the hfs to the nuclear quadrupole hamiltonian.[6]

$$E(Q) = -\chi_{aa} Y(JIF). \qquad (2)$$

The J = 3→4 and all higher J→J′ transitions are complicated by hfs from non-zero K states. The presence of only K=0 for the J = 2→3 transition suggests 3-fold or higher symmetry due to the off axis bosons $^{12}C$ and $^{16}O$ of $CO_2$.[7] The presence of three $CO_2$'s and a three fold symmetry axis is proven by the observation of K = +/-3 hfs for J = 3→4. Table II summarizes the line centers and residues to a fit of the hf transition frequencies for $HCN(CO_2)_3$.

From these fits it is clear that there is not a noticeable dependence of $\chi$ on J or K, in contrast to $HCN(CO_2)_2$.[2]

Once the $C_3$ symmetry was proven, initial estimates of the rotational constants of the isotopically substituted tetramers involving $HC^{15}N$, $H^{13}CN$, and DCN were made using the parallel axis theorem.[7] The $(CO_2)_3$ subunit was assumed to be planar with $I_b$ and $I_c$ for it as previously determined. [1] One then has,

$$I_b = \mu R_{c.m.}^2 + I_b((CO_2)_3) + I_b(HCN) \tag{3}$$

where $\mu$ is the reduced mass of the pseudo-dimer comprised of HCN and $(CO_2)_3$, $R_{c.m.}$ is the distance from the c.m. of HCN to the c.m. of the cyclic $(CO_2)_3$, and $I_b(HCN)$ and $I_b((CO_2)_3)$ are the moments of inertia of HCN and $(CO_2)_3$ (Table VII). [1,7,8]

Rotational transitions were found for the isotopically substituted tetramers and demonstrated that the N was weakly bonded to the cyclic $(CO_2)_3$ subunit with the H furthest away from the $(CO_2)_3$. This was evidenced by the fact that the transitions for the DCN substituted complex were much lower in frequency than the corresponding transitions for the $HC^{15}N$ substituted complex (Table III). This is due to the fact that the H is farther away from the c.m. of the complex than the N and substitution of it effected a greater increase in the moment of inertia of the complex. This leads to lower rotational constants (Table V) and hence lower frequency transitions. Line centers for $HCN(CO_2)_3$ and the other symmetric top species are shown in Table III.

Rotational transitions were found for the $HCN(^{13}CO_2)_3$ species, also a symmetric top. This species breaks the $K = +/- 3n$, $n = 0,1,2...$, rule and again gives evidence for $C_3$ symmetry.

In order to determine the pinwheel angle, $\beta$, the symmetry of the complex had to be broken. Transitions of $HCN(^{18}OCO)(CO_2)_2$, with the outer O substituted, were observed and the rotational constants fit to the spectra obtained. The transitions were attributed to the species with the outer O substituted because the transitions which were observed were

relatively close to those predicted for it based on the already determined geometry. The line centers and rotational constants for HCN($^{18}$OCO)($CO_2$)$_2$ are given in Table IV.

Structural Determination

The $B_o$'s for the mono-isotopically substituted HCN species (Table V) enable us to determine an $R_s$ substitution structure for HCN by using the Kraitchman equation for single substitution on the axis of a linear or symmetric top molecule, [6]

$$I_b' - I_b + \mu_i c_i^2 \qquad (4)$$

where the prime indicates the substituted species, $I_b$ is the moment of inertia of the parent species given by $I_b \times B_o = 505379$ uÅ$^2$MHz, $\mu_i$ is the reduced mass of the substitution, and $c_i$ is the distance along the c axis of the substituted atom, i, from the c.m. of the parent molecule. The $c_i$ values are averaged over the zero point vibrations, which are assumed to be unchanged by substitution. For HCN, the vibrations are largely the bending oscillations of the relatively rigid monomer about its center of mass (c.m.), and the positions are the projection onto the c axis at its average angular displacement, $\theta$, as seen in Figures 1 - 3. This enables us to determine $\theta$ in HCN as for a linear dimer. [9,10]

$$R_s(d) - R_s(m)\cos\theta \qquad (5)$$

where $R_s$(m) is the substitution bond distance observed in the free monomer and $R_s$(d) is the projected value in the pseudo-dimer.

The atomic positions, bond distances, and torsional amplitude for HCN are determined this way and the values are given in Table VI. The position of the outer H in HCN is poorly determined because of the large effects of deuterium on vibration, but the C-N bond distance of 1.1364 Å should be reliable. Using equation (5), with the corresponding C-N bond distance of HCN in the free monomer of 1.15512 Å, we find the torsional amplitude, $\theta$, for HCN to be 10.3°.

If the free monomer value of $\chi_o(m)$ did not change upon complex formation, then the projection operator,

$$\chi_c(t) = 0.5\chi_o(m)(3cos^2\theta - 1) \tag{6}$$

could be used to determine $\theta$ from $\chi_o(m)$, the quadrupole interaction constant of the free monomer HCN, and $\chi_c(t)$, the projection of the quadrupole interaction constant along the molecular axis, which is experimentally determined from a fit of the hfs. Using the values of $\chi_o(m)$ and $\chi_c(t)$ from Tables I and VII, we determine $\theta$ to be 19.9°, a value significantly larger than the 10.3° from the substitution method. This difference is explained by the charge redistribution effects of complex formation and the corresponding change in the electric field at the N nucleus, which changes the value of the quadrupole interaction constant.[9] A value of -4.087 was obtained for $\chi_o(c)$, the complexed quadrupole interaction constant, from the experimental $\chi_c(t)$ value and the angle $\theta$ from the substitution method. This is significantly different from the value of -4.7091 reported for the free monomer HCN, [9] with $\Delta\chi$ = .622 MHz (a 13.2% change).

The substitution positions of HCN enable us to find $R_{c.m.}$, the c.m. to c.m. separation of the two subunits (Figures 1 - 3). $R_{c.m.}$ may be determined from $B_o$ with the following expression for the moment of inertia of a linear dimer in which HCN oscillates isotropically about its c.m.,

$$I_b = \mu R_{c.m.}^2 + I_b((CO_2)_3) + 0.5I_b(HCN)(cos^2\theta + 1) \tag{7}$$

where $\mu$ is the reduced mass of the complex treated as pseudodiatomic. $R_{c.m.}$ is determined by subtraction of this relation with the same relation for an isotopically substituted species of HCN,

$$I_b' = \mu' R_{c.m.}'^2 + I_b((CO_2)_3) + 0.5I_b'(HCN)(cos^2\theta + 1) \tag{8}$$

$I_b((CO_2)_3)$ remains constant and falls out of the final expression. In the substitution relation, the actual $R'_{c.m.}$ is

$$R'_{c.m.} = R_{c.m.} + D \tag{9}$$

where D is the change in the c.m. of HCN upon substitution. With this method, and using the normal isotopic species as parent, an average value of 2.7580 Å is determined for $R_{c.m.}$ from the three values for the symmetric top species, excluding $DCN(CO_2)_3$.

The C-C distance in the $(CO_2)_3$ subunit (Figures 1 and 2) may be determined from the $B_o$ value for $HCN(^{13}CO_2)_3$ by using Kraitchman's equations for off-axis multiple substitution retaining $C_3$ symmetry,[6]

$$\Delta I_y = \Delta I_x \quad 1.5\Delta m y^2 + \mu_s z^2 \tag{10}$$

where $\Delta I_y$ and $\Delta I_x$ are the changes in moments of inertia due to substitution, $\Delta m$ is the change in mass due to substitution, y is the distance of each substituted atom off the $C_3$ symmetry axis, z is the distance from the substituted atom to the c.m. of the complex, and $\mu_s$ is the reduced mass of the substitution. The value of z can be determined from $R_{c.m.}$ because the carbons are coplanar with the c.m. of the $(CO_2)_3$ subunit. Therefore, z is $R_{c.m.}$ less the distance from the c.m. of the complex to the c.m. of HCN. This gives a value of z 0.4685 Å. By substituting this in equation (10), we find y to be 2.1922 Å, which is the distance from the c.m. of the $(CO_2)_3$ subunit to the C. By symmetry, the corresponding C-C distance is 3.7970 Å.

This leaves the angles $\gamma$, the out-of-plane rotation, and $\beta$, the in-plane rotation, to be determined (Figures 1 - 3). To help accomplish this, analytical expressions were derived for the moments of inertia of the $(CO_2)_3$ subunit in $HCN(CO_2)_3$. For the symmetric top species, there is no dependence of the overall moments on the value of $\beta$. The final expressions were,

$$I_a = I_b = 2m(CO_2)(R_{CC}/2)^2 + 1.5I(CO_2)(1 + sin^2\gamma) \tag{11}$$

$$I_c = m(CO_2)R_{CC}^2 + 3I(CO_2)cos^2\gamma \qquad (12)$$

where $R_{CC}$ is the C-C distance in the $(CO_2)_3$ subunit, m($CO_2$) is the mass of $CO_2$, I($CO_2$) is the moment of inertia of free $CO_2$, and $\gamma$ is the out of plane angle. The value of $\gamma$ can be determined from these expressions using the observed $B_o$ values, and an average value (over all symmetric top species except DCN$(CO_2)_3$) of $\gamma = 36.41°$ was obtained.

The position of the outer oxygen can be determined from the rotational constants of HCN($^{18}$OCO)$(CO_2)_2$ through Kraitchman's equations for substitution off the symmetry axis.[6] The equations call for the moments of inertia along the molecular axes, $I_x$, $I_y$, and $I_z$, but the moments along the inertial axes, $I_b$, $I_a$, and $I_c$, were substituted respectively. Using this approach, we obtained values of /z/ = 0.0931 and /y/ = 2.8664 Å. These are the distances of the substituted atom from the c.m. of the complex. The value for z shows that the outer O is rotated up toward the HCN because its value, positive or negative, corresponds to the outer O to being above the C-C-C plane.

To determine the out-of-plane bend, $\gamma$, the distance of the outer O to the C-C-C plane is needed. The distance from the C-C-C plane to the c.m. of the complex is 0.4685 Å (Table VI), so the distance to the outer O is 0.4685 +/- /z/ Å. $\gamma$ is related to this distance by the expression,

$$d = R_{C-O}sin\gamma \qquad (13)$$

where d is the distance from the C-C-C plane to the outer O, and $R_{C-O}$ is the C-O bond distance. This gives values of $\gamma = 28.9°$ (z = +0.0931 Å) or $\gamma = 18.8°$ (z = -0.0931 Å). Neither agrees very well with the value determined from the inertial expressions ($\gamma = 36.41°$), but the value of $\gamma = 28.9°$ is closer and will be used as the substitution value of $\gamma$.

$\beta$ can be determined from the value of /y/ and the angle $\gamma$. $\beta$ is related to these two parameters by the trigonometric expression,

$$y^2 = (R_{C=O}cos\gamma)^2 + r^2 - 2(R_{C=O}cos\gamma)rcos(90 - \beta) \quad (14)$$

where $R_{C=O}$ is the C=O bond distance and r is the distance from the C of $CO_2$ to the symmetry axis. Using the substitution value of $\gamma = 28.9°$, a value for $\beta$ of 32.2° was obtained. Using $\gamma = 36.41°$ from the inertial analysis, $\beta$ was determined to be 38.2°. The discrepancy between the values of $\gamma$ as determined by the substitution method vs. the inertial analysis may be explained by the fact that the c.m. of the complex is displaced off of the symmetry axis upon substitution, and that the oscillations of the $CO_2$'s are not necessarily isotropic with respect to the rotated inertial axes. This anisotropy could have a significant effect due to the large amplitude vibrations of the $CO_2$'s.

## DISCUSSION

There are four structural parameters in $HCN(CO_2)_3$ which need to be discussed with respect to its subunits, $(CO_2)_3$ and HCN, and its lower order analogs, $HCN(CO_2)_2$ and the T-shaped $HCNCO_2$. These parameters are $R_{CN}$, the carbon of $CO_2$ to nitrogen distance, $R_{CC}$, the carbon to carbon distance in $(CO_2)_3$, $\gamma$, the out of plane rotation of the $CO_2$'s, and $\beta$, the in plane rotation of the $CO_2$'s. Free $(CO_2)_3$ has been observed to be a planar species (with $\beta$ not determined experimentally); whereas in the tetrameric $HCN(CO_2)_3$ the $(CO_2)_3$ subunit has its oxygens rotated out of the C-C-C plane by 36.4°. The $R_{CC}$ distance is shorter than in free $(CO_2)_3$ by 0.2412 $\AA$ and the $R_{CN}$ distance is greater than in $HCN(CO_2)_2$ by 0.7200 $\AA$ and in the T-shaped $HCNCO_2$ by 0.7970 $\AA$. The $\chi_{gg}$ value along the molecular axis is also very different from the dimer, -3.891 MHz in the tetramer as compared to -4.075 MHz in the dimer, demonstrating extensive perturbation of the electric field at the N nucleus, with a change in $\chi_o$(m) of 13.2%.

The structural changes brought about in $(CO_2)_3$ by interaction with HCN are due primarily to electrostatic effects. $CO_2$ has no permanent dipole moment but it does have a large electric quadrupole moment with the oxygens having a partial negative charge and the carbon having a positive charge of twice that magnitude. HCN has a strong dipole moment with the nitrogen having a partial negative charge. Thus, the formation of $HCN(CO_2)_3$ can be viewed as the result of the attraction of the N of HCN to the C's of the $(CO_2)_3$ subunit.

The three inner oxygens of $(CO_2)_3$ are closest to the $C_3$ axis and therefore closest to the nitrogen. The inner O's are rotated away from the HCN to reduce the repulsion between the the O's and the N. $R_{CC}$ is reduced in $(CO_2)_3$, which in itself is an unfavorable interaction since the three carbons repel each other, but this is compensated by having the three positive C's closer to the $C_3$ axis and therefore closer to the N. $R_{CN}$ is greater than in the T-shaped dimer, which again is in itself an unfavorable interaction since the optimum distance is that

of the dimer, but this is compensated by increasing the distance between the nitrogen and the outer O's which are rotated toward the HCN. Therefore the final values of $R_{CN}$, $R_{CC}$, $\gamma$, and $\beta$ are due to the optimization of the C-N attraction and the minimization of the C-C, N-O(inner), and N-O(outer) repulsions.

Due to the $C_{3h}$ pinwheel configuration of $(CO_2)_3$, concurrent rotation of the three $CO_2$'s in or out of the C-C-C plane, $\beta$ or $\gamma$, respectively, does not affect the symmetry of the complex. Moreover, the rotational constants of all of the symmetric top species do not depend on the sign of $\gamma$ nor on the value of $\beta$. Therefore, the symmetry had to be destroyed to determine this information.

$\beta$ was determined to be 32.2° (substitution method) or 38.2° (substitution value of /v/ with inertial value of $\gamma$). Both of these are less than Fraser's value of 43°. This result indicates that there is an O(inner)-O(inner) repulsion which must be taken into consideration. Since the C-C distance was reduced, the inner O's were also brought closer together. A decrease in the angle $\beta$ would serve to separate the inner O's from each other, but it would also bring the outer O's closer to the N. $\beta$ is therefore affected by a minimization of these two repulsions.

The $R_{CC}$ and $R_{CN}$ distances vary greatly between the dimeric, trimeric, and tetrameric species of $HCN(CO_2)_m$ (m = 1,2,3). The values of $R_{CC}$ are 1.7530 Å for the trimer (m = 2) and 3.7970 Å for the tetramer (m = 3). The values for $R_{CN}$ are 3.00, 2.1201, and 4.3507 Å for m = 1, 2 and 3, respectively. These results are in direct contrast to other complexes such as $Ar_mHCl$ (m = 1,2,3), where the Ar-Ar and Ar-HCl distances remain relatively constant over all species.[7] This is most probably due to the electrostatic interactions of $CO_2$ and the geometrical implications of the oxygens.

The quadrupole interaction constant along the molecular axis, $\chi_{gg}$, of $HCN(CO_2)_3$ agrees favorably with that determined for $HCN(CO_2)_2$.[2] Both, however, exhibit significant charge redistribution effects, as demonstrated by the value of $\theta$ determined by the substitution

method vs. the value determined with the projection operator method. In the latter, the value of $\chi_o(c)$ (the quadrupole interaction constant of complexed HCN) differs significantly from $\chi_o(m)$ (the quadrupole interaction constant of free HCN)(Eq. 6) due to the change in electric field. This charge redistribution effect was not considered by Leopold, et al, [3] who used the experimental value of $\chi_a(d)$ and the unperturbed value of $\chi_o(m)$ to determine the torsional angle of HCN in the T-shaped $HCNCO_2$ dimer. This value of the torsional angle could be greatly affected by charge redistribution and a substitution analysis is needed to determine these effects. In the tetramer, the charge redistribution effects are significant, with the value of $\chi_o(m)$ decreased by 13.2%.

Another interesting aspect of the $HCN(CO_2)_n$ species is the effect of centrifugal distortion on $\chi_{gg}$. In the T-shaped dimer, no effect was conclusively reported although the data might indicate a slight dependence on the value of K, the difference falling within the 5% error margin and therefore ignored. In $HCN(CO_2)_2$, there is a definite dependence of $\chi_{gg}$ on the value of K but there is no dependence in the tetramer (Table I).

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Figure 1. Structure of the $HCN(CO_2)_3$ tetramer based on the obtained spectra.

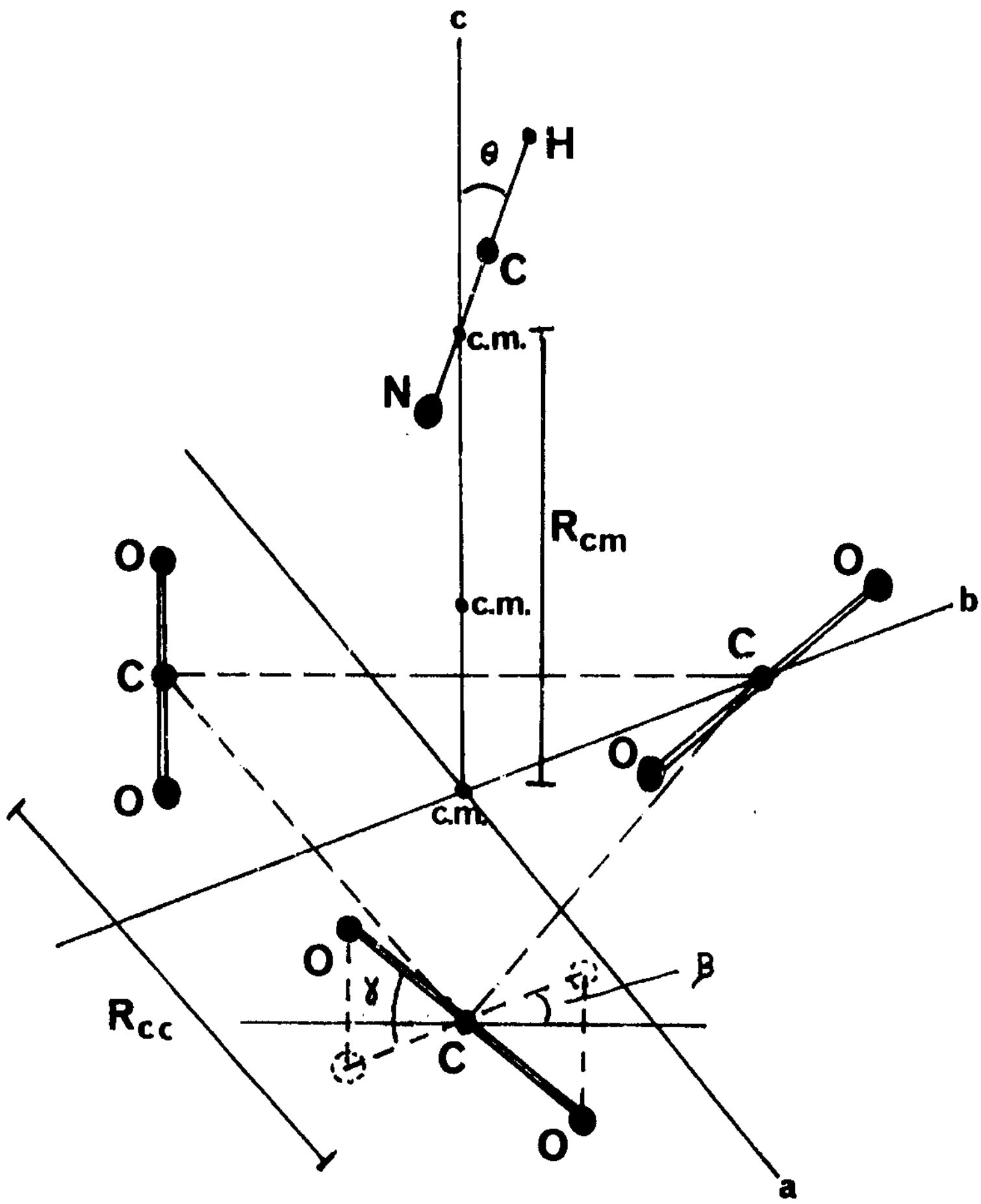

Figure 2. View of $HCN(CO_2)_3$ along the c axis. The figure shows the in plane bend, $\beta$, and $R_{CC}$. Dimensions are to scale.

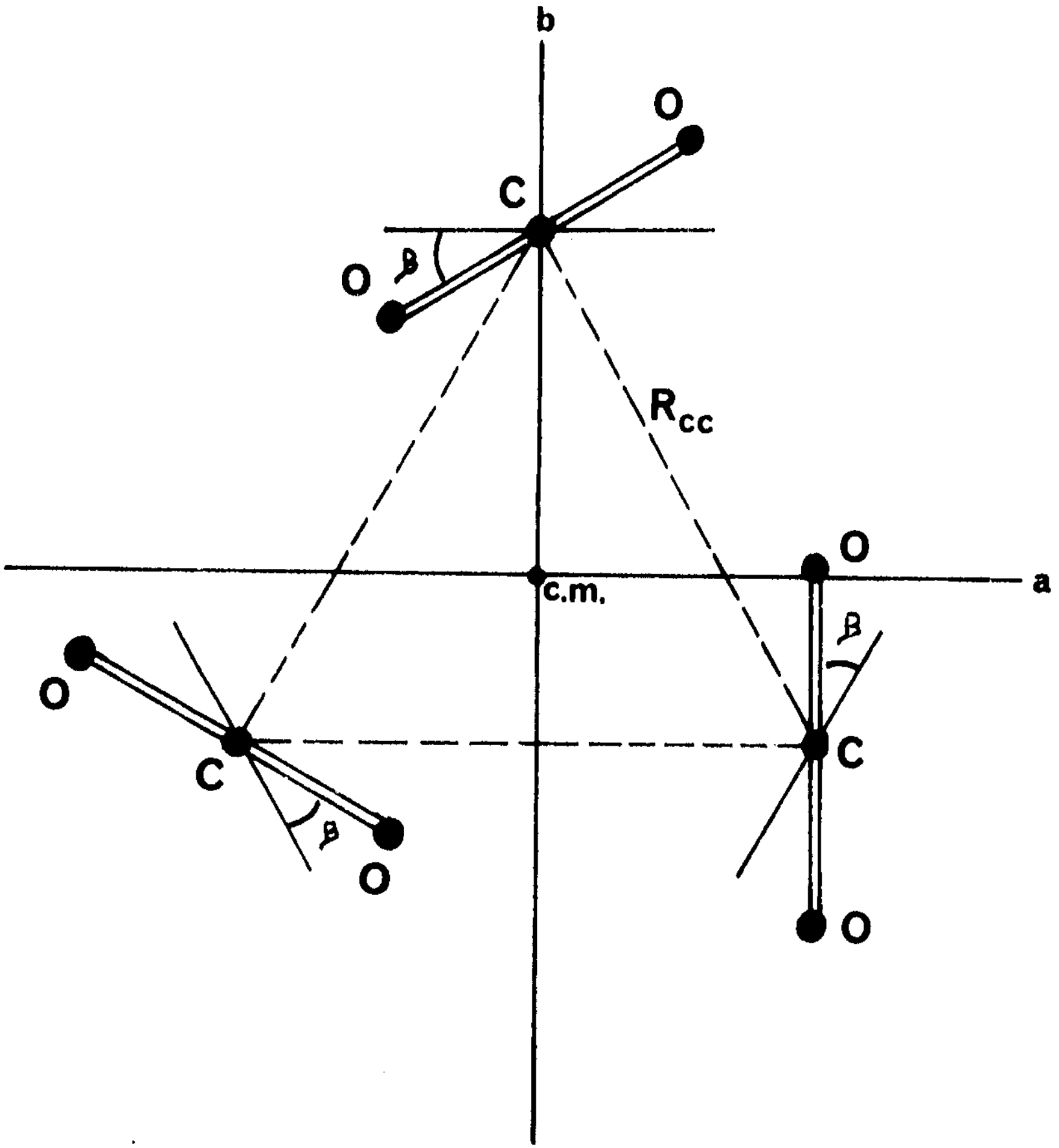

Figure 3. View of $HCN(CO_2)_3$ along the b axis. The figure shows the out of plane bend, $\gamma$, the HCN torsional angle, $\theta$, and $R_{cm}$. Dimensions are to scale.

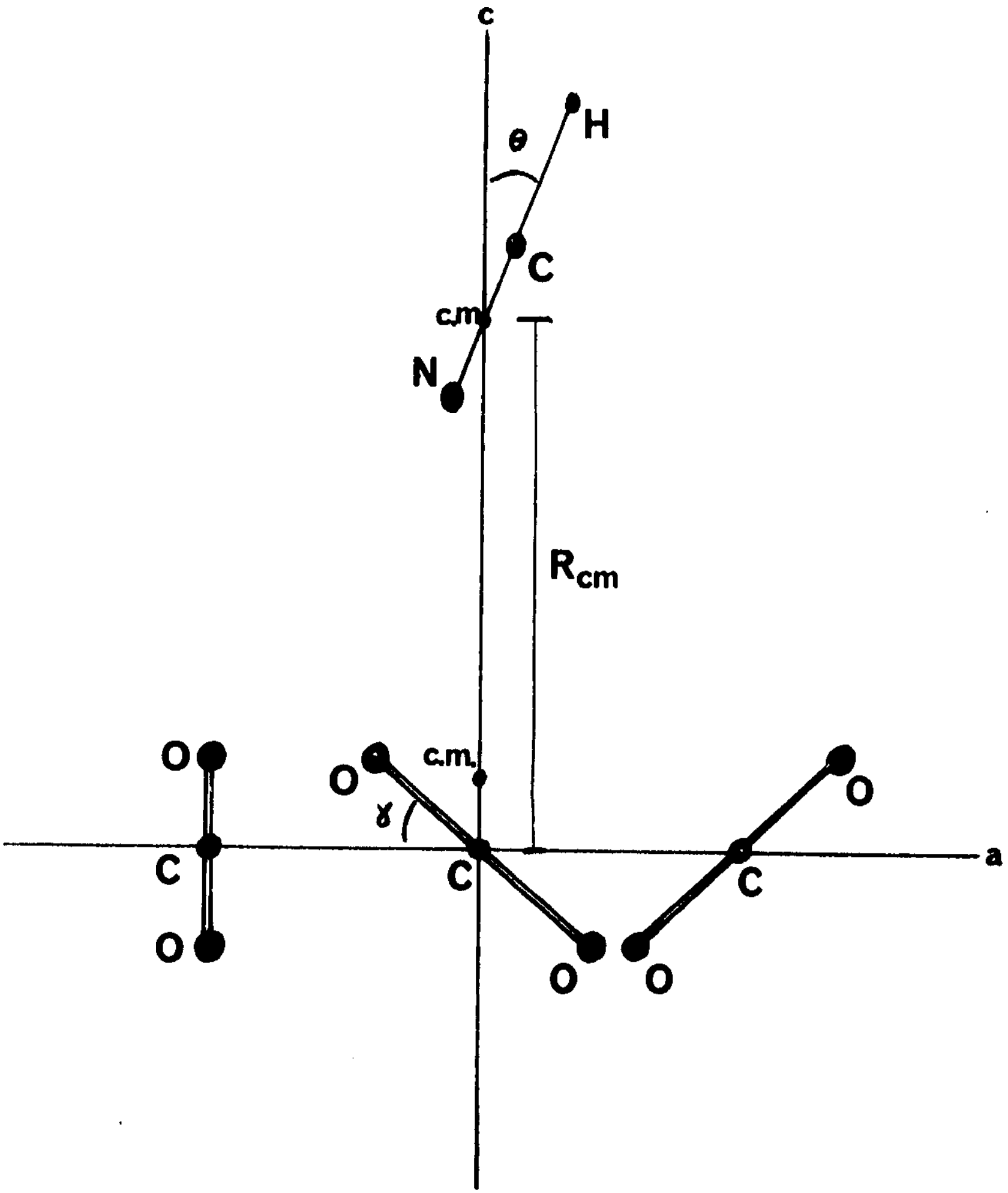

Table I: Representative Hyperfine Structure of $HCN(CO_2)_3$

| J 2 3 ; K = 0 | | | |
|---|---|---|---|
| F - F' | Obs. (MHz) | Calc. (MHz) | Δ (MHz) |
| 2 - 1 | 5168.5110 | 5168.5120 | -0.0010 |
| 3 - 3 | 5169.5700 | 5169.5681 | 0.0019 |
| 1 - 1 | 5169.7625 | 5169.7626 | -0.0001 |
| 2 - 2 | 5169.8085 | 5169.8089 | -0.0004 |
| 1 - 3 | 5171.5130 | 5171.5135 | -0.0005 |

| J 3 - 4 ; K = 0 | | | |
|---|---|---|---|
| F - F' | Obs. (MHz) | Calc. (MHz) | Δ (MHz) |
| 2 - 1 | 6891.6410 | 6891.6418 | -0.0008 |
| 3 - 3 | 6892.8545 | 6892.8551 | 0.0006 |
| 1 - 1 | 6892.9314 | 6892.9385 | -0.0071 |
| 2 - 2 | 6892.9772 | 6892.9680 | 0.0092 |
| 1 - 3 | 6894.6049 | 6894.6057 | -0.0008 |

| J 3 - 4 ; K = 1/-3 | | | |
|---|---|---|---|
| F - F' | Obs. (MHz) | Calc. (MHz) | Δ (MHz) |
| 1 - 3 | 6891.4258 | 6891.4248 | 0.0010 |
| 1 - 1 | 6892.0047 | 6892.0067 | -0.0020 |
| 2 - 2 | 6893.1623 | 6893.1600 | 0.0023 |
| 3 - 3 | 6893.6054 | 6893.6067 | -0.0013 |

TABLE II: Line centers and $\chi_{cc}$ values for $HCN(CO_2)_3$

| J - J' : K | Line Center (MHz) | $\chi_{cc}$ |
|---|---|---|
| 2 - 3 ; 0 | 5169.7626 (1.0)* | -3.891 |
| 3 - 4 ; 0 | 6892.9385 (-0.7) | -3.890 |
| 3 - 4 ; 3 | 6892.8794 (-0.7) | -3.879 |
| 4 - 5 ; 0 | 8616.0513 (-0.1) | -3.880 |
| 4 - 5 ; 3 | 8615.9780 (0.5) | -3.876 |

* Numbers in ( ) are observed - calculated values for the line centers. Values are given in kHz.

Table III: Line Centers for symmetric top species of $HCN(CO_2)_3$

| J-J'; K | $HCN(CO_2)_3$ | $HC^{15}N(CO_2)_3$ | $H^{13}CN(CO_2)_3$ | $HCN(^{13}CO_2)_3$ | $DCN(CO_2)_3^{\dagger}$ |
|---|---|---|---|---|---|
| 2-3 ; 0 | 5169.7626 (1.0)* | 5144.5330 (0.6) | 5099.8379 (6.4) | 5101.2185 (-2.0) | ------ |
| 2-3 ; 1 | ------ | ------ | ------ | 5101.2177 (2.0) | ------ |
| 3-4 ; 0 | 6892.9385 (-.7) | 6859.3021 (3.1) | 6799.7061 (-3.8) | 6801.5510 (-1.8) | ------ |
| 3-4 ; 1 | ------ | ------ | ------ | 6801.5486 (2.2) | ------ |
| 3-4 ; 3 | 6892.8794 (-0.7) | 6859.2452 (-4.0) | 6799.6323 (-4.8) | 6801.4948 (-.4) | ------ |
| 4-5 ; 0 | 8616.0513 (-0.1) | 8573.9962 (-2.9) | 8499.5313 (0.9) | ------ | 8398.4732 (-2.6) |
| 4-5 ; 3 | 8615.9780 (0.5) | 8573.9402 (3.2) | 8499.4451 (3.9) | ------ | ------ |
| 5-6 ; 0 | ------ | ------ | ------ | ------ | 10078.1378 (4.0) |
| 6-7 ; 0 | ------ | ------ | ------ | ------ | 11757.7700 (-1.6) |

*Numbers in ( ) are Obs. - Calc. for line centers.

Values are given in kHz.

†Values for $DCN(CO_2)_3$ are only estimated from hfs.

Table IV: Line centers and rotational constants for HCN($^{18}$OCO)($CO_2$)$_2$

| Transition | Frequency (MHz) |
|---|---|
| $2_{11} - 3_{21}$ | 5066.4779* |
| $2_{02} - 3_{12}$ | 5091.1247 |
| $2_{12} - 3_{22}$ | 5099.8806 |
| $2_{20} - 3_{30}$ | 5108.6726 |
| $2_{21} - 3_{31}$ | 5136.1127 |

| Rotational constant | Value |
|---|---|
| A (MHz) | 861.6165* |
| B (MHz) | 838.3704 |
| C (MHz) | 668.3626 |
| $D_{jk}$ (kHz) | 0.5307 |
| $D_k$ (kHz) | -1.196 |

* Residues and SDP's were not calculated since only five transitions were observed and five parameters were determined.

NOTE: $D_J$ was not determined since all transitions are $J = 2 \rightarrow 3$.

A value of $D_J$ = .681 kHz (parent) was used in the fit.

Table V: Rotational Constants for symmetric tops of $HCN(CO_2)_3$

| | $HCN(CO_2)_3$ | $HC^{15}N(CO_2)_3$ | $H^{13}CN(CO_2)_3$ | $HCN(^{13}CO_2)_3$ | $DCN(CO_2)_3^*$ |
|---|---|---|---|---|---|
| $B_o$(MHz) | 861.6392 (2)[+] | 857.4345 (9) | 849.9824 (14) | 850.2154 (8) | 839.8546 (10) |
| $D_j$(kHz) | 0.681 (5) | 0.692 (23) | 0.584 (33) | 0.666 (30) | 0.1407 (1) |
| $D_{jk}$(kHz) | 0.821 (12) | 0.691 (57) | 1.010 (82) | 0.890 (51) | ..... |

*Values for $DCN(CO_2)_3$ are based on apx. line centers

[+]Numbers in ( ) are SDP values.

Table VI: Substitution positions and bond distances in $HCN(CO_2)_3$[a]

| Atom | Position y-axis (Å) | Position z-axis (Å) | Bond | Distance (Å) |
|---|---|---|---|---|
| H | 0 | 3.9005 | | |
| C | 0 | 2.8404 | H-C | 1.0601 |
| N | 0 | 1.7040 | C-N | 1.1364 |
| O (outer) | 2.8664 | 0.0931 | $R_{c.m.}$ | 2.7580 |
| C | 2.1922 | 0.4685[b] | monomer | angle |
| O (inner) | not | determined | HCN | 10.3° |

[a]Based on $B_o$ values in Table V and Rotational Constants in Table IV with normal isotopic species as parent.

[b]This value was based on the First Moment condition ($\sum_i m_i r_i = 0$) and on $R_{c.m.}$. It was not determined experimentally.

Table VII: Properties of the subunits, HCN and $(CO_2)_3$.

| HCN[a] | | $(CO_2)_3$[b] | |
|---|---|---|---|
| Property | Value | Property | Value |
| $B_o$ (MHz) | 44315.9757 | B (MHz) | 1193.4380 |
| $r_s$ H-C (Å) | 1.06317 | C (MHz) | 596.7190 |
| $r_s$ C-N (Å) | 1.15542 | $R_{C'C}$ (Å) | 4.0382 |
| $\chi_{aa}$ (MHz) | -4.7079 | | |

[a] Refs. 8 and 11

[b] Ref. 1